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Effect of copper doping on phosphorescence of CaS : Er phosphors

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Abstract : CaS phosphors doped with varying concentrations of Er and / or Cu (singly as well as doubly activated) were prepared The phosphorescence have been studied with reference to the phosphorescence decay characteristics and the spectral distribution of luminescence emission The present study is confined to the effect of higher concentration of Cu (1% to 10^{-2} %) on CaS phosphors activated with very low concentration of Er (10^{-4} to 10^{-9} %) The decay study reveals that the trap group corresponding to about 0.69 eV is independent of activator concentration and is characteristic of the host lattice itself CaS . Er phosphor gives a characteristic band at 5750 Å , while CaS.Cu gives two bands at 4440 and 5800 Å The phosphorescence spectra of doubly activated CaS:Er, Cu phosphors again give two bands at 4440 and 5800 Å. Blue, green and red emission is of great interest for color displays, printing, opto-electronics, lasers, medical diagnosis and of therapeutical use.

Keywords : CaS·Er phosphors, copper doping, phosphorescence

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1. Introduction

In order to elucidate information about luminescence process of phosphors, the knowledge of defect structures and the distribution of energy levels in the band gap of solids is very essential and as such, the aim of the present work is to investigate the phosphorescence characteristics, the type of kinetics involved, decay law, and the trap distribution *etc.*

Rothschild [1] in 1958 reported that no luminescence was found with Er alone while secondary activators such as Cu could be made to luminescence. Phosphorescence is interpreted as a tunneling recombination between holes and electrons trapped, respectively by cation vacancies (V centers) and unidentified donor centers [2].

It was found that un-activated phosphor did not show any luminescence while the luminescence is observed when the base is activated with either Er or Cu or other activators. The multiple activators Er and Cu used in the present study, give rise to the same emission band at 5750 Å. This would indicate that the emission is due to a native defect in the host crystal such as cation or anion vacancy. Since the activators introduced are cations, they could produce sulfur vacancies. Investigations by many other workers on alkaline earth sulfide phosphors in this laboratory also supports this view.

2. Preparation and experimental procedure

Phosphors were prepared by firing the mixture of sodium thiosulphate as a flux in high grade gypsum powders as host lattice along with A.R. grade carbon powder (Riedal, Germany) as the reducing agent in proper proportions. The varying amount of activator, erbium (erbium oxide obtained from Johnson Matthey & Co., Halton Garden, London EC 1) and/or copper (as cupric sulfate from British Drug House Ltd, Poole-England) is added to this above mixture and the charge is fired at 900°C for 2 hours. Then it is pulverized in a dry atmosphere and stored, keeping in view the extreme purity as the main consideration in the preparation.

2.1. Phosphorescence spectra

The phosphorescence spectra of the doubly-doped CaS:Er, Cu phosphors were photographed using the Steinheil Raman Spectrograph (Model GH Universal) U. V. lamp was the source of excitation. The sample holder for the study of phosphorescence consists of a cylindrical pyrex tube of uniform

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diameter and thickness which encloses another ebonite tube 'E'. By having this type of arrangement, the surface area of the phosphor sample could be increased without requiring a large quantity of phosphor powder. Another advantage of this arrangement was that since the diameter of the phosphor holder was fairly large, no stray light from its surface could reach the spectrograph slit. The slit width was the same as in that of fluorescence study. Ilford R-40 photographic plates were used for both fluorescence and phosphorescence study. To calibrate the spectra, an iron spectrum was used as the standard spectrum. The time of exposure for phosphorescence for all the samples was kept two hours to cover up all phosphors weak as well as strong. The intensity of the phosphorescence was measured on a G II- Micro-photometer aided with an automatic recorder "CARL ZEISS JENA".

2.2. *Phosphorescence decay*

Phosphors were excited by ultraviolet lamp (UVS-12, made in U.S.A.), emitting predominantly 3650 Å. To maintain excitation energy constant, a stabilizer was also used in conjunction with the lamp. The photo-multiplier tube operated at 900 V obtained from a well stabilized D. C. power supply. The output of the photo-multiplier tube was connected to the potentiometric recorder (CARL-ZEISS-JENA). It was found that four minutes excitation was sufficient to excite the phosphor to the saturation value and as such for each phosphor, exciting light was switched off after 4 minutes and immediately the shutter of the photo-multiplier tube carefully removed while recording the decay. Thus, intensity as a function of time was plotted by the plotter giving decay curves on a recorder. All the measurements were made at room temperature.

In the case of phosphors having long duration phosphorescence, traps always play a fundamental role as in the present case. These phosphors usually exhibit a power law decay such as

$$I = I_0 t^{-b}, \tag{1}$$

where I is the phosphorescence intensity at time t, I_0 that at $t = 0$ and b is the decay constant [3]. In case of distribution of trapping levels, phosphorescence is due to superposition of intensities, each varying exponentially with time. The decay curve thus obtained by plotting logarithm of intensity (I) as a function of time (t), is then hyperbolic. In such cases of distribution of trapping levels, the observed intensity will be due to their superposition of all the exponentials and the form of the curve can be represented by the above eq. (1)

Randall and Wilkins [3] suggest that the complex hyperbolic decay in the sulfide type of phosphors can be explained by the monomolecular mechanism as in the simple case, but with a distribution of trap depths. They considered the thermal release of trapped electrons as the main determining process (and hence the monomolecular kinetics) and assumed that no re-trapping derived the form of decay for several distribution of trap depths.

First order kinetics is a recombination dominant process. In this process, re-trapping is practically negligible in comparison to recombination. This is the process which is frequently observed and widely reported in the literature. In second order kinetics, recombination and re-trapping processes take place with equal probability. The decay is fastest in first order kinetics Second order kinetics is found to be more slowly decaying

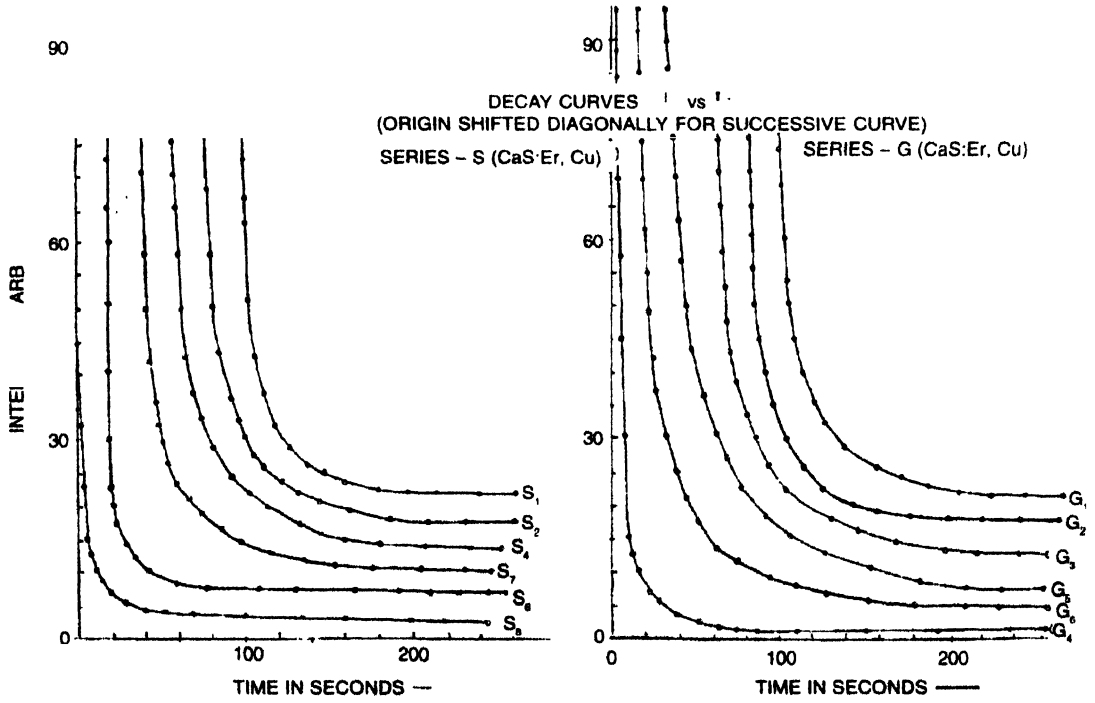

Figure 1. Plot of phosphorescence intensity *vs* time.

process than the first order kinetics and the third order kinetics decays more slowly than the second order kinetics and so on. The extent of recombination and re-trapping process decides on the order of kinetics involved. With increasing order of kinetics, the extent of recombination decreases with a simultaneous increase in the extent of re-trapping [4].

3. Results and discussion

3.1 *Analysis of decay curves*

In the present studies, the observed decay curves are hyperbolic in nature. Decaying intensity (I) is plotted against time (t). I *vs* t plots showed hyperbolic rather than exponential nature (Figure 1). Therefore, the possibility of simple exponential decay with a single trap was ruled out. Log I *vs.* t plots did not give the expected straight lines. The log I *vs* t curve was found to be concave upwards (Figure 3 : peeling off of decay curves). However, a log – log plots of phosphorescence intensity *vs* time were very nearly straight lines as shown in Figure 2 which helps in concluding that phosphoric decay characteristics (P.D.C.) is hyperbolic in nature but the slope is not equal to two which is the case for second order kinetics. The value of correlation coefficient calculated for all the samples comes out to be nearly equal to 1 showing linear relationship between log I and log t.

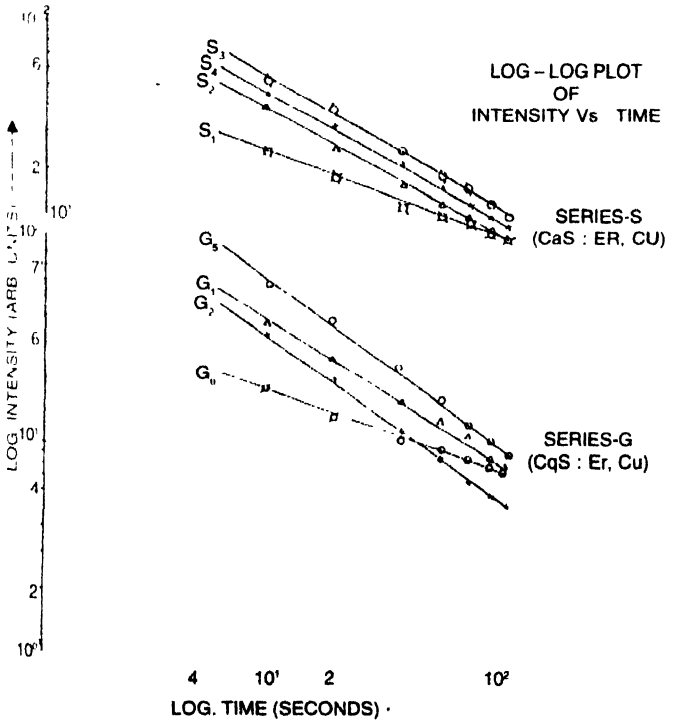

Figure 2. Log – Log plot of intensity *vs.* time.

As the number of exponentially distributed traps increases, the decay takes the form of hyperbolic nature due to their superposition. Superposition of trapping levels at different energies makes the emission complicated. The degree of linearity therefore is estimated by evaluating the correlation coefficient r, the value of which is close to unity. Such type of PDC can be represented by a power law as suggested by Randall and Wilkins [3]. They considered hyperbolic decay as the result of superposition of exponentials corresponding to different traps. Corresponding to these components, three different trap depths are obtained by using the equations :

$$I = I_0 \exp(-pt), \tag{2}$$

$$p = S. \exp(-E/kT), \tag{3}$$

where p is the probability of escape of electrons from traps per sec., S is the attempt to escape frequency (here 10^9/sec for alkaline earth sulfide phosphors [5]), E is the trap depth, k the Boltzmann constant and T the absolute temperature.

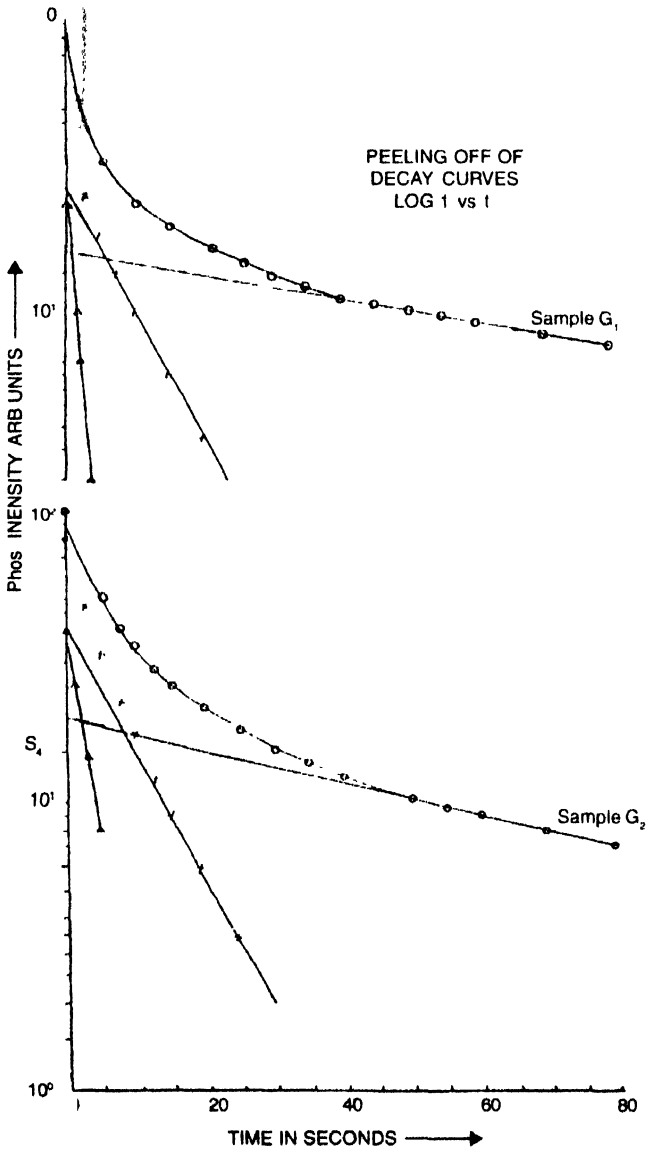

Figure 3. Peeling off of decay curves (log I *vs* t)

As the hyperbolic decay is considered to be the result of superposition of exponentials corresponding to different depths, following Bube [6] and others, the decay curves were analyzed into three exponentials by the method of successive subtraction (peeling off of decay curves). In such phosphors,

the first stage decays very rapidly and then is followed by another slow decay component and all the stages are exponential in nature. The different components of the decay may be considered as due to traps of different depths. As the number of exponential distributed traps increases, the decay takes the form of hyperbolic nature due to their superposition. The minimum number of exponentials required to do so can be three. Thus, it is reasonable to assume that as the number of exponentials increases, the decay curve changes from a straight line to a hyperbolic curve on a semi-log plot. The peeling off of curves are concave upwards because shallow traps empty soon leading to rapid initial phosphorescence decay while the deeper traps will be responsible for the long duration phosphorescence; thus traps go on emptying with time eventually leaving the slower components which correspond to deeper traps approaching to three exponentials which were calculated using the 'peeling procedure'. The result of this method is quite satisfactory. The values of E calculated by peeling off of decay curves are tabulated and are termed as slow, middle and fast components (Table 1).

A fast component decline in intensity is followed by a slower one. The shallow traps decay rapidly, emptying with time, leaving the slower component of deeper traps. At longer intervals, when shallow traps are more or less exhausted, deep traps start contributing to phosphorescence intensity at a slower rate. Consequently, the decay constant may vary with time provided the traps of different depths contribute appreciably to the after glow intensity at room temperature. Since the phosphorescence in inorganic phosphors is due to absorption of electrons below conduction band, the thermal energy at room temperature is sufficient to empty the shallow traps which therefore, become ineffective in phosphorescence decay. The decay measurements at room temperature thus pertain only to electron traps that are relatively deep.

Table 1. Values of trap depth, correlation coefficient and decay constant of decay curves

Samples series	Erbium Er (%)	Copper Cu (%)	Decay constant (−b)	Correl. coef (−r)	Trap depth E in eV Slow	Middle	Fast
A 9	5×10^{-4}	NIL	0 29	0 99	0 63	0 60	0 54
A 11	5×10^{-5}	NIL	0.31	0.99	0.69	0.60	0 57
A 12	1×10^{-5}	NIL	0 24	0 99	0.69	0.60	0 56
A 15	5×10^{-7}	NIL	0.42	0.99	0.67	0.60	0 58
A 17	5×10^{-8}	NIL	0 37	1.00	0.67	0.60	0.56
B 1	NIL	1	0.35	0.98	0 62	0 60	0.56
B 2	NIL	5×10^{-1}	0 38	0 98	0 70	0 60	0 57
B 3	NIL	1×10^{-1}	0 53	0 98	0.66	0 60	0 56
B 4	NIL	5×10^{-2}	0 46	0.98	0 67	0 60	0 58
B 5	NIL	1×10^{-2}	0 38	0.99	0 67	0 60	0 57
C 1	1×10^{-5}	1	0.47	0.99	0 66	0.60	0 55
C 2	1×10^{-5}	5×10^{-1}	0.48	0.99	0.67	0 61	0 56
C 3	1×10^{-5}	1×10^{-1}	0 50	0.99	0 66	0 60	0 56
C 4	1×10^{-5}	5×10^{-2}	0.52	0 99	0.68	0 61	0 55
S 1	5×10^{-7}	1	0.35	0.99	0 68	0 60	0 55
S 2	5×10^{-7}	5×10^{-1}	0.46	0 99	0.68	0 61	0 58
S 3	5×10^{-7}	1×10^{-1}	0 52	0 99	0 67	0 61	0 57
S 4	5×10^{-7}	5×10^{-2}	0 53	0.99	0.66	0 60	0 55
G 1	5×10^{-8}	1	0.61	0 99	0 66	0 60	0 59
G 2	5×10^{-8}	5×10^{-1}	0.61	0.98	0 67	0 60	0 57
G 3	5×10^{-8}	1×10^{-1}	0.74	0.99	0.65	0 60	0 55
G 4	5×10^{-8}	5×10^{-2}	0.77	0.99	0.64	0 58	0 55

Trap depth does not depend on the activator concentration (Figure 4). It was found that the introduction of activator affects the distribution of trap levels responsible to phosphorescence. A slight variation in the trap depths could be due to the perturbation caused by the activators in the distribution of trap densities. However, the variation is so small that the overall variation can be assumed to be negligible. Hence, the possibility remains that the activators may give rise to very shallow or very deep traps. Negligible variation of trap-depths with the activator concentration indicates that the trapping levels in these phosphors are due to defects in the host lattice and these defects are likely to be the sulfur vacancies. This is in agreement with the findings of other workers.

Traps of different depths contribute to the phosphorescence intensity at different times. The traps which contribute phosphorescence have depth in the region of 0.54, 0.60 and 0.69 eV as calculated from the three exponentials fast, middle and slow. The trap depths thus obtained are found in good agreement with those obtained from glow curves, thus justifying the use of Randall and Wilkins mono-molecular theory and the use of the fundamental eq. (3) which indicate that the kinetics involved is likely to be mono-molecular.

The value of decay constant b calculated by the method of least squares is much less than unity (Table 1). The small variation of decay constant with activator concentration suggests that the activator only modifies the relative importance of the trap but not their mean depth. Hence, the distribution of traps can be assumed to be quasi-uniform. The variation of decay constant with activator concentration implies proper growth of micro-crystalline powder phosphors.

The correlation coefficient r, the values of which are close to unity with a negative sign indicating that the relationship between log I and log t is almost linear. The negative sign implies that the intensity diminishes with time. The sign of b comes out to be negative hence the observed hyperbolic decay can be represented by the above eq. (1).

The phosphorescence decay, thermo-luminescence and fluorescence studies reveal that there is only one group of traps having depth in the region of 0.54 to 0.69 eV, which can be associated with host lattice defects. This is further supported by many other workers that the electron traps (trap group corresponding to about 0.68 eV) are independent of the impurity ions and formed by the crystalline imperfections in the lattice.

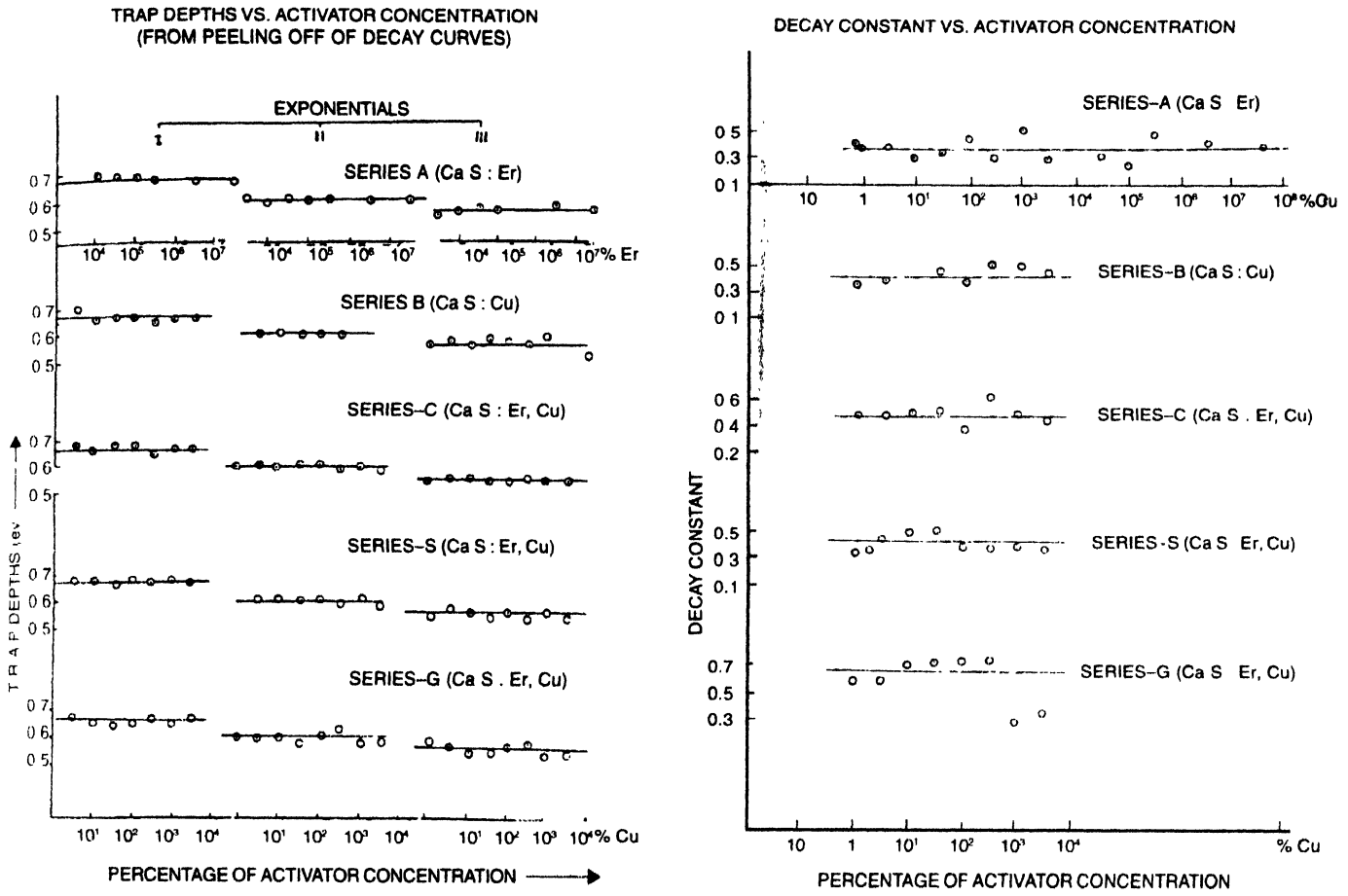

Figure 4. Trap depths *vs* activator concentration, and decay constant *vs* activator concentration

3.2 Phosphorescence spectra studies

A-Series (CaS : Er^{3+}) : A phosphorescence band in the yellow-orange region at about 5750 Å (2.14 eV) is clearly seen, as observed in the case of fluorescence study. Blue band is not prominent in any of the samples. As the concentration of Er decreases to 5×10^{-4} % (sample A 9), an intense bell-shaped band in the yellow-orange region grows fully at 5750 Å, till it reaches the optimum concentration of 10^{9} % (sample A 19) similar to that observed in fluorescence (except a few with higher concentration of erbium beyond 10^{-2}%, where the band is resolved into a group of Er-lines at 5520, 5545, 5570, 5615 Å *i.e.* 2.23 to 2.20 eV are clearly visible, confirming the incorporation of Er in CaS host lattice which agrees well with the group of lines observed by Lehmann [7] with 1% Er with CaS base material

Table 2. Peak wavelength and relative intensity of phosphorescence bands).

Series Samples	Erbium Er (%)	Copper Cu (%)	Band in blue region Peak wavelength Å	Rel. Intensity Arb Unit	Band-yellow-orange regn. Peak wavelength Å	Rel. Intensity Arb Unit
A 12	1×10^{-5}	NIL	–		5800	51
A 16	1×10^{-7}	NIL	–	–	5740	52.5
A 17	5×10^{-9}	NIL	–	–	5760	45 5
B 1	NIL	1	–	–	5800	57
B 2	NIL	5×10^{-1}	4560	8.5	5800	62.5
C 1	1×10^{-5}	1	4720	6	5714	46 5
C 2	1×10^{-5}	5×10^{-1}	4440	16	5770	48 5
C 3	1×10^{-5}	1×10^{-1}	4440	1	5750	27
S 1	5×10^{-7}	1	4720	8	5790	61
S 2	5×10^{-7}	5×10^{-1}	4327	8 5	5790	59
S 3	5×10^{-7}	1×10^{-1}	–	–	5790	28 5
G 1	5×10^{-8}	1	4469	1	5730	11
G 2	5×10^{-8}	5×10^{-1}	4442	3	5730	46 5

at 2.23 eV). No shift is observed. It would appear fairly reasonable that the materials showing band emission have compensated the presence of the trivalent rare- earth with a defect, as for example, vacancy and it is this combination that is involved in the energy state responsible for the band emission. Keller and Petit [8] also pointed that around the rare-earth ion, one could have a lattice perturbed by a vacancy.

B-Series (CaS :Cu^{2+}) : Two bands at 4440 and 5800 Å are seen. As the concentration increases, a shift towards shorter wavelength is observed (samples B 1–B 4). The intensity curves of fluorescence and phosphorescence bands with higher concentration show that the intensity is very high indicating the formation of luminescence centers. This confirms the incorporation of Cu-ions in the host lattice.

C, S and G-Series (CaS : Er^{3+}, Cu^{2+}) : In all the samples of these series, two bands, one in the blue region at 4440 Å (2.8 eV) and the other in the yellow-orange region at 5750 Å (2.14 eV) are seen (Figures (5-7)). The bands with higher concentration are quite intense (samples C1-C3) whereas the bands with lower concentration were quite weak in intensity (samples C5-C7).

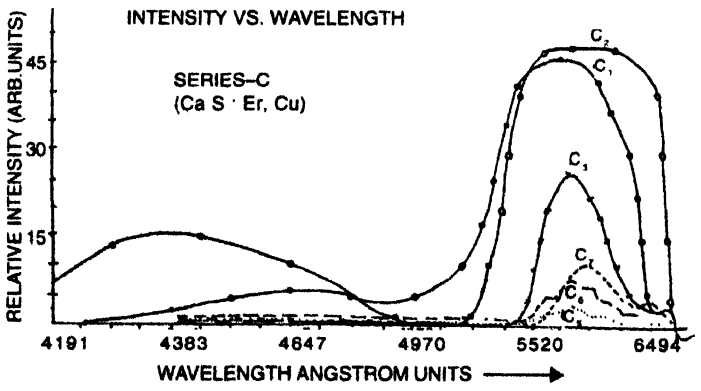

Figure 5. Phosphorescence spectra of Series C : CaS : Er, Cu phosphors.

The bands in the blue region seem to be suppressed with decrease in copper concentration. With decreasing concentration of copper, both the bands at 4440 and 5750 Å go down. Increase in Er-content slightly broadens the band particularly with higher Cu-content (Figure 5). A slight shift of the blue phosphorescence band relative to the fluorescence band is also seen, whereas the position of the yellow-orange band in all the series remains unaffected.

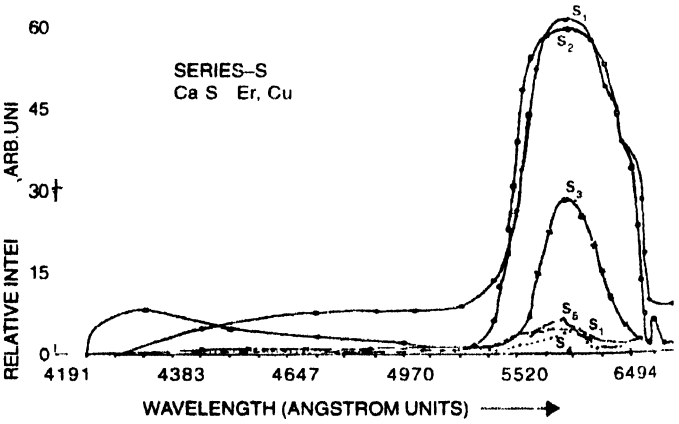

Figure 6. Phosphorescence spectra of Series S · CaS . Er, Cu phosphors

In G-Series, where the Er-concentration is further decreased (5×10^{-8}% Er), the bands of the phosphors co-doped with a low concentration of copper seems to be enhanced in intensity as seen in fluorescence as well. The presence of two activators produces a sensitivity to stimulation which is not obtained with either activator alone. Brightness of phosphors seems to increase with copper content, indicating that copper may be responsible for enhancing the emission. With copper alone quenching is obtained in the concentration range in which copper sensitizes the erbium activated CaS phosphors as seen in fluorescence. Band at 5050 Å seen in fluorescence, is not

observed at all in phosphorescence spectra. It is justified to assume that the blue emissions are characteristics of Cu-activator and the yellow-orange emission may be due to sulfur vacancies. This is in agreement with the findings of Van Gool [9] who suggested that the orange emission in CaS:Ag originates in the presence of either silver or sulfur vacancies or of the two kinds of defects in association.

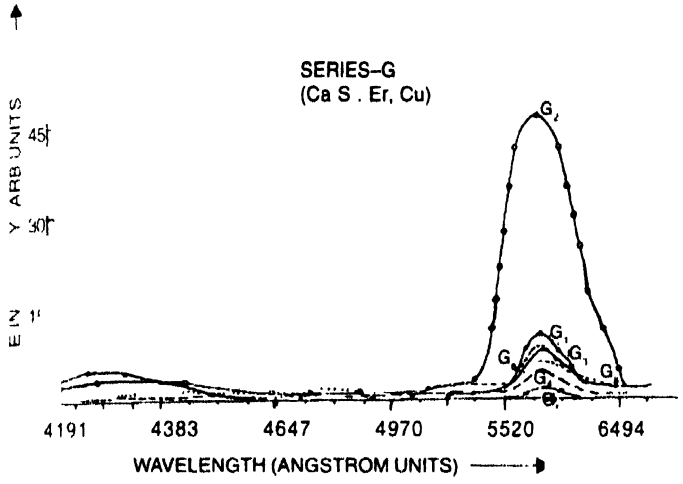

Figure 7. Phosphorescence spectra of Series G CaS Er, Cu phosphors

Besides, a large number of sulfur vacancies are produced in CaS particularly under the experimental conditions in which these phosphors are prepared. These can also serve as charge compensators in the present case. Lehmann [7] stressed on the point that as there can be no reason to expect the principle of charge compensation to be invalid for CaS phosphors, it can be assumed that the luminescence center does not consist only of activator and co-activator ions replacing ions of the host crystal but is more complicated possibly involving interstitials and/or vacancies as well.

The multiple activators used separately in fluorescence study, give rise to the same emission band at 5750 Å. This would indicate that the emission is due to a native defect in the host crystal such as a cation or anion vacancy. Ivey square law fits the position of the bands with CaS, SrS and BaS. It must be due to sulfur vacancies. Its strong temperature dependence suggests as an evidence of native defect. Therefore, the observed band at 5750 Å (2.14 eV) may be attributed to sulfur vacancies which might be created during the incorporation of the activators (Er_2O_3 and $CuSO_4$) used with the base material CaS [10].

The decay and polarization studies by Shinoya [11] and ESR studies by de Bruin *et al* [12] also presented strong evidence for Cu and S association in R-Cu luminescence and supported the Shinoya model. The presence of centers analogous to F-centers is recognized in CaS.

The introduction of Cu for calcium produces an acceptor level. As such, one should expect an association between the acceptor level due to Cu and a neighbouring sulfur vacancy which acts as a donor. The donor-acceptor transition may be responsible for the blue emission. The sulfur vacancy can also behave in a manner similar to an F-center except that it carries a positive charge. The yellow-orange band may be similar to F-center luminescence. Ekbote's [13] results with self-activated CaS phosphors also supports the above view Calcium produces a number of S vacancies and thus defect centers. It can reasonably be assumed that anion vacancies (sulfur vacancies) can create F^+ or F^- aggregate centers in CaS phosphor as suggested by other workers. The production of S vacancies seem to be related to the metallic character of the activators. The band at 2.1 eV observed by Ekbote with or without activator is also seen in the present case. This band is reported with different activators by many other workers also.

Hence, it may be concluded that the band at 5750 Å (2.14 eV) may be due to negative ion vacancy centers. This discussion leads to inference that the luminescence of the present system of phosphors seem to be due to defect centers (analogous to F-centers) and activator centers.

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